

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Poly lactam Products and Methods for their Production

We THE POLYMER CORPORATION, a Corporation of the Commonwealth of Pennsylvania, United States of America, of 2120 Fairmont Avenue, Reading, State of Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of poly lactam products. More specifically, it deals with the incorporation of so-called microspheres in poly lactams by including such microspheres in higher lactams and polymerising the lactams by low temperature anionic polymerisation processes while the microspheres are uniformly distributed throughout the polymerising mass. This has the effect of obtaining poly lactam product having reduced density.

The term "microsphere" has become known to those skilled in the art as pertaining to hollow spherical particles generally ranging from 30 to 300 microns in diameter. They can comprise glass, phenolic resin or urea formaldehyde. A preferred type is of glass and is sold commercially by Emerson & Cuming, Inc. under the Trade Mark "Eccosphere". These glass spheres have a light weight, low dielectric constant, low dissipation factor, high temperature stability and low thermal conductivity, which makes them ideal as fillers for nylon. They have a bulk density of about 18.0 lbs/cu.ft.

It has been found that poly lactams having reduced density can be formed in which the physical properties of the poly lactams are not seriously compromised. These poly lactams are formed by incorporating microspheres in the poly lactam to obtain a reduced density, variable within moderately wide limits, while still maintaining high strength and durability.

According to the invention there is provided a process of producing poly lactam product by means of the low temperature anionic polymerisation of a reactive lactam monomer with a promoter and catalyst as herein described, comprising adding the microspheres to the monomer while the monomer is in a state permitting uniform dispersion of the microspheres and polymerising the monomer to obtain a solid poly lactam having the microspheres uniformly dispersed in it.

The polymers referred to in this invention are poly lactams prepared by low temperature anionic polymerisation. By low temperature polymerisation is meant polymerisation below the melting point of the polymer and above the melting point of the monomer. Due to the low melt viscosity of most poly amides, a uniform dispersion of microspheres is difficult to achieve in poly amides. Even if good dispersion of the fillers in the polymer is obtained, it is difficult to maintain such dispersion during subsequent shape formation, such as injection molding and extrusion, which necessarily entails exceeding the melting point of the poly amide.

Due to the fact that the low temperature anionic polymerisation processes can be conducted below the melting point of the polymer and can be carried out with extreme rapidity, it is possible to mix the microspheres with the monomer until the viscous stage of the polymerisation is reached and thus insure a uniform distribution of the microspheres in the resulting shaped poly lactam.

Briefly, the invention relates to the polymerisation of higher lactams, i.e. lactams containing at least 6 carbon atoms in the lactam ring, as for example, ϵ -caprolactam, enantholactam, caprylolactam, decanolactam, undecanolactam, dodecanolactam, pentadecanolactam, hexadecanolactam, methylcyclohexanone isoximes, cyclic hexamethylene adipamide, and mixtures thereof; in the presence of an

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anionic polymerisation catalyst, as for example, alkali and alkaline earth metals such as lithium, sodium, potassium, magnesium, calcium, strontium, either in metallic form or in the form of hydrides, borohydrides oxides, hydroxides, carbonates, organo-metallic derivatives of the foregoing metals, as well as other metals, such as butyl lithium, ethyl potassium, propyl sodium, phenyl sodium, triphenylmethyl sodium, diphenyl magnesium, diethyl zinc, triisopropyl aluminum, diisobutyl aluminum hydride, sodium amide, magnesium amide, magnesium anilide, Grignard reagent compounds, such as ethyl magnesium chloride, methyl magnesium bromide, phenyl magnesium bromide and a promoter compound such as organic isocyanates, ketenes, acid chlorides, acid anhydrides, and N-substituted imide having the structural formula $A-N-B$, as disclosed in specification R 914,022. The promoter compound preferably has a molecular weight of less than 1000.

This polymerisation of the higher lactams is initiated at temperatures of from the melting point of the lactam monomer to 250°C, and preferably from 125° to 200°C. As the reaction is exothermic, the initiation temperature will be exceeded under most conditions. The amount of catalyst and promoter compound each can vary from 0.01 to 20 mole percent, preferably from 0.05 to 5 mole percent, and more preferably still from 0.1 to 1 mole percent, all based on the higher lactam being polymerized. The higher lactams preferably contain from 6 to 20 carbon atoms and more preferably contain from 6 to 12 carbon atoms. The anionic catalyst preferably is a Grignard compound or an alkali metal or hydrides thereof. It will be understood that the anionic catalyst can be reacted in stoichiometric amount with a higher lactam to form a salt thereof, such as sodium caprolactam, and said salt can then be employed in the polymerization process in an equivalent amount to the anionic catalyst as set out hereinabove. This preliminary preparation is particularly desirable as it permits ready removal of hydrogen gas from the system when sodium or sodium hydride is employed, removal of water when sodium hydroxide is employed, and removal of water and carbon dioxide when sodium carbonate is employed.

Isocyanates and N-substituted imides are the preferred promoter compounds. It will be understood that the use of acid chlorides effects the presence of HCl in the system which preferably is removed therefrom to preclude reaction with the anionic catalyst, whereby extra catalyst would otherwise be required. Similarly acid anhydrides generate organic acids in the system which then require sufficient anionic catalyst to neutralize the organic acid in addition to the amount de-

sired to function in the polymerization reactions.

Beside glass microspheres, microspheres of urea-formaldehyde resin or phenol-formaldehyde resin may be used. Due to the low temperature at which polymerization takes place, many types of microspheres can be used as long as the melting point of the spheres is above the temperature at which polymerization takes place.

Basically, the process of the present invention consists of including these microspheres in a reactive lactam monomer containing a catalyst and a promoter, heating said monomer to the temperature where polymerization occurs and letting it polymerize to a solid while the microspheres are uniformly distributed therein.

It has been found that the convection currents caused by the heat applied to the monomer and the exothermic nature of the polymerization process, disperses the microspheres uniformly throughout the monomer, which may, in part, eliminate the necessity of mechanical agitation prior to the time the polymerizing mass becomes sufficiently viscous to prevent gravity separation.

The process outlined above is more specifically illustrated by the following examples:

EXAMPLE I

Into ε-caprolactam monomer was added about 50%, on a dry volume basis, of glass microspheres. (Eccospheres) The caprolactam containing the microspheres was heated to about 169°C., during which time the microspheres were uniformly dispersed in the monomer due to the convection currents caused by the heating apparatus. Polymerization was then initiated by adding 1/200 molar quantity of a sodium hydride catalyst and 1/200 molar quantity of a tolylene diisocyanate promoter. A solid polycaprolactam article was formed containing microspheres uniformly dispersed throughout. The density of the resulting rigid product was about 0.81 as opposed to a normal density of about 1.15 for a solid polycaprolactam article.

EXAMPLE II

The experiment of Example I was repeated this time using 10% by volume glass microspheres. A rigid polycaprolactam product was formed having a density of about 1.06.

EXAMPLE III

15% by volume phenol-formaldehyde resin microspheres were added to ε-caprolactam. The microspheres had a particle size of about 40 microns, had a real density of about 0.25, were nitrogen filled, and were sold by Union Carbide under the Trade Mark Bakelite Phenolic Micro Balloons BJO-0930.

The above mixture was polymerized using a 1/400 molar quantity of sodium hydride

and a 1/200 molar quantity of tolylene diisocyanate. The reaction was initiated at about 160°C. The product produced by such polymerization was a rigid polycaprolactam having a density of about 0.97.

WHAT WE CLAIM IS:—

1. A process of producing polylactam product by means of the low temperature anionic polymerisation of a reactive lactam monomer with a promoter and catalyst as herein described, comprising adding microspheres to the monomer while the monomer is in a state permitting uniform dispersion of the microspheres and polymerising the monomer to obtain a solid polylactam having the microspheres uniformly dispersed in it.

2. A process according to claim 1, comprising adding the microspheres to the monomer, heating the monomer thereby dispersing the microspheres by means of the convection currents caused by the heating, initiating polymerisation by the addition of the catalyst and

the promoter and permitting completion of polymerisation.

3. A process according to claims 1 or 2, in which said microspheres are selected from the group consisting of glass spheres, spheres of phenol-formaldehyde resin, and spheres of urea-formaldehyde resin.

4. A process according to claim 1, 2 or 3, wherein said microspheres are added in the amount of from 10—50% by volume on a dry basis.

5. A method according to claim 1 for making a polylactam product substantially as herein described with reference to the Examples.

6. A polylactam product whenever produced by the method of any one of the preceding claims.

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